Low Temperature Crystallization Process is the Key to ZLD Without Chemical Conditioning

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ABSTRACT: A vacuum crystallization process operated at low temperature has been developed based on crystallization techniques used in the salt, chemical, and fertilizer industries. It is being applied in wastewater treatment and recycle to achieve zero liquid discharge for some difficult waste streams including FGD scrubber blowdown, coal gasification grey water, shale gas frac and produced water, and landfill leachate.

Environmental regulations are looming which may have the practical effect of requiring zero liquid discharge (ZLD) wastewater treatment in a large number of industries. This means that the industrial wastewater is reduced to a solid which is usually landfilled. Any recovered water from the ZLD treatment process is recycled and reused in the plant. Typically the wastewater is pre-concentrated in a membrane process such as reverse osmosis; an evaporator; or both. The concentrated wastewater is then reduced to a solid product using a crystallizer, dryer, or solar evaporation pond.

Physical and chemical properties of the wastewater, energy usage, emissions produced, and permitting requirements determine which combination of unit operations will result in the most practical and cost-effective treatment process. The concentration and chemical properties of the species present in the wastewater, whether dissolved, suspended, or emulsified, often pose processing problems in these varied unit operations. These often relate to scaling, fouling, foaming, corrosion, air emissions, and extreme process conditions (temperature, pressure, pH). Often additional physical or chemical pre-treatment steps make sense in developing a ZLD treatment process to mitigate these adverse effects.

In the last 40 years or so, several trends have influenced the design of ZLD wastewater treatment plants. They include the development and advancement of various membrane-based technologies; the application of electrically-driven Mechanical Vapor Recompression (MVR) to evaporators and crystallizers to dramatically improve energy usage; use of seed slurry scale mitigation techniques in falling film type evaporators; the application of industrial crystallization techniques; strict regulations

and permit requirements for air emissions from dryers; and liners and monitoring wells required for evaporation ponds.

These technologies can be roughly ranked in order of increasing CAPEX and OPEX: evaporation ponds, membranes, evaporators, crystallizers, and dryers. Membranes and evaporators are the workhorses for water removal and recovery, but only ponds, crystallizers and dryers can reduce wastewater to solids suitable for landfill disposal. Ponds and dryers require permits from regulators to operate, which are often difficult or impossible to obtain. Membrane systems are made of plastic materials; evaporator and crystallizers are made of corrosion-resistant alloys. Therefore, the process of choice for ZLD wastewater treatment systems has evolved into membranes followed by seeded MVR evaporator and crystallizer. The evaporator and crystallizer are operated at atmospheric pressure to minimize the size of the alloy process vessels.

Unfortunately, there are several waste streams produced in common industrial processes that have been regarded as too difficult and/or too costly to treat in the traditional ZLD process described above. These include blowdown from FGD limestone scrubbers, grey water from coal gasification processes, shale gas frac and produced water, and landfill leachate. These are all examples of waste streams containing high concentrations of total dissolved solids (TDS) in the 30,000 to 100,000 mg/L range. The dissolved salts are mainly highly soluble chloride or nitrate salts.

These streams have too high a dissolved salt concentration to obtain any significant water recovery with membranes. Evaporators can generally recover 50-75% of the water in these streams, but are limited by the solubility of sodium salts and high boiling point rise. Crystallization of the salts contained in these streams is very difficult due to their very high solubilities and resulting boiling temperatures and their tendency to hydrolyze at high temperature, releasing acid. The process vessels in which crystallization is carried out can be very expensive due to extreme process conditions of high temperatures and pressures and low pH.

In the past, elaborate chemical treatment schemes including softening and clarification, ion exchange, steam stripping and other unit operations have been used to change the basic chemical make-up of the salts in the wastewater to make a solution more amenable to the traditional ZLD process. Often these unit operations require large quantities of chemicals and energy to pre-treat and condition the wastewater. Further, there is the associated expense and logistics of bringing in bulk chemicals by the truckload or rail car load, storage and mixing of chemicals, solids separation and dewatering, and transporting and landfilling the dewatered sludge.

For example, the purge stream from wet limestone FGD scrubbers is a wastewater composed mainly of calcium and magnesium chloride, saturated in calcium sulfate. It also contains toxic and/or hazardous constituents such as metals, mercury, selenium, and boron. Existing ZLD treatment plants for FGD wastewater use chemical softening of the scrubber blowdown prior to evaporation. Conventional lime-soda ash softening is used to remove most of the magnesium and calcium ions in the scrubber blowdown as precipitates of magnesium hydroxide and calcium carbonate. The net result of the softening process is that sodium ions are substituted for most of the calcium and magnesium ions and some of the metals.

The softened scrubber blowdown becomes mainly an aqueous solution of sodium chloride. The softener sludge must be settled and dewatered and is disposed of in a landfill. The softened scrubber blowdown is then evaporated in an MVR falling film evaporator and water is recovered. The final concentration is done in an atmospheric crystallizer, in which the sodium chloride crystallizes. A slurry of crystals and mother liquor is discharged from the crystallizer into a centrifuge or pressure filter. A wetcake of sodium chloride and a small amount of mother liquor is discharged. The mother liquor in the wetcake contains the remaining toxins from the scrubber wastewater. The wetcake is disposed in a landfill.

Figures 1A and 1B show a typical flow diagram for a ZLD system for wet limestone FGD purge water using lime-soda ash softening as pretreatment to an evaporator and crystallizer with solids dewatering.

Treatment of shale gas frac and produced waters in a ZLD process is similar to the process described above for limestone FGD purge, as the chemistry is similar – mainly calcium, magnesium, and sodium chloride with lesser amounts of potassium, barium, and strontium. Calcium, magnesium, barium, and strontium are all highly soluble as chloride salts, difficult to crystallize, but can all be replaced with sodium using conventional lime-soda ash softening.

For gasification grey water, the main salt is ammonium chloride, another highly soluble acid salt difficult to crystallize at atmospheric pressure. Caustic stripping has been used to replace the ammonium ion with sodium ions, so that a sodium chloride solution is sent to an evaporator and crystallizer system. The stripping process requires sodium hydroxide as a source of sodium ions and to raise the pH to convert ammonium ions to ammonia,

and steam to remove the ammonia from solution as a gas.

A unique low temperature crystallization process known as the Cold Process (Crystallization Of High Solubility Salts at Low Temperature and Deep Vacuum) eliminates the need to pretreat or chemically condition these difficult waste streams. Energy and capital costs for the cold crystallization process are comparable to current evaporation and crystallization technology, but there are huge savings in chemical and sludge disposal costs by eliminating the need for pretreatment.

The cold crystallization process is a very simple process, essentially the traditional ZLD process. It is the only method which results in direct crystallization of highly soluble salts, including chlorides, nitrates, and salts of organic acids. The cold process is operated under vacuum at low temperature in order to take advantage of the reduced solubility and boiling point rise of high solubility salts at lower temperature.

Cold crystallization is a common process in industrial salt crystallization, having been widely applied over the last half century in the production of such chemicals as sodium carbonate decahydrate from trona; sodium sulfate decahydrate (Glauber's salt) for detergent use; chloride salts of calcium, magnesium potassium, lithium, and ammonium from natural brine deposits; nitrate salts of ammonium, sodium, and strontium in the fertilizer and chemical industries; and salts of organic acids such as glyphosate, the main ingredient in the herbicide Roundup. In the production of all of the above-mentioned salts, the final crystallization of the salt is done in vacuum crystallizers to take advantage of the reduced solubility and boiling point elevation of the desired salt at low processing temperature.
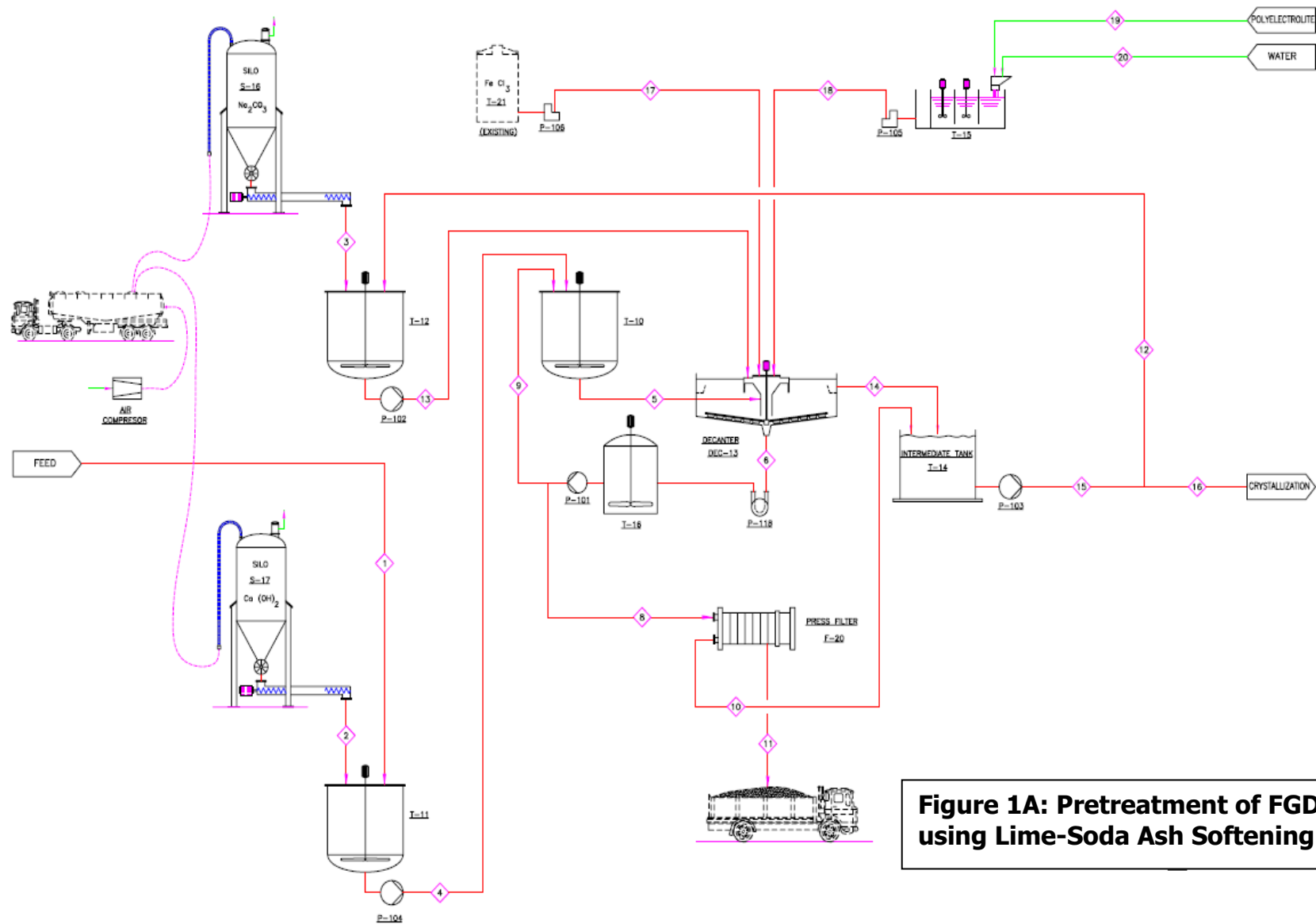
Figure 1A: Pretreatment of FGD Purge using Lime-Soda Ash Softening
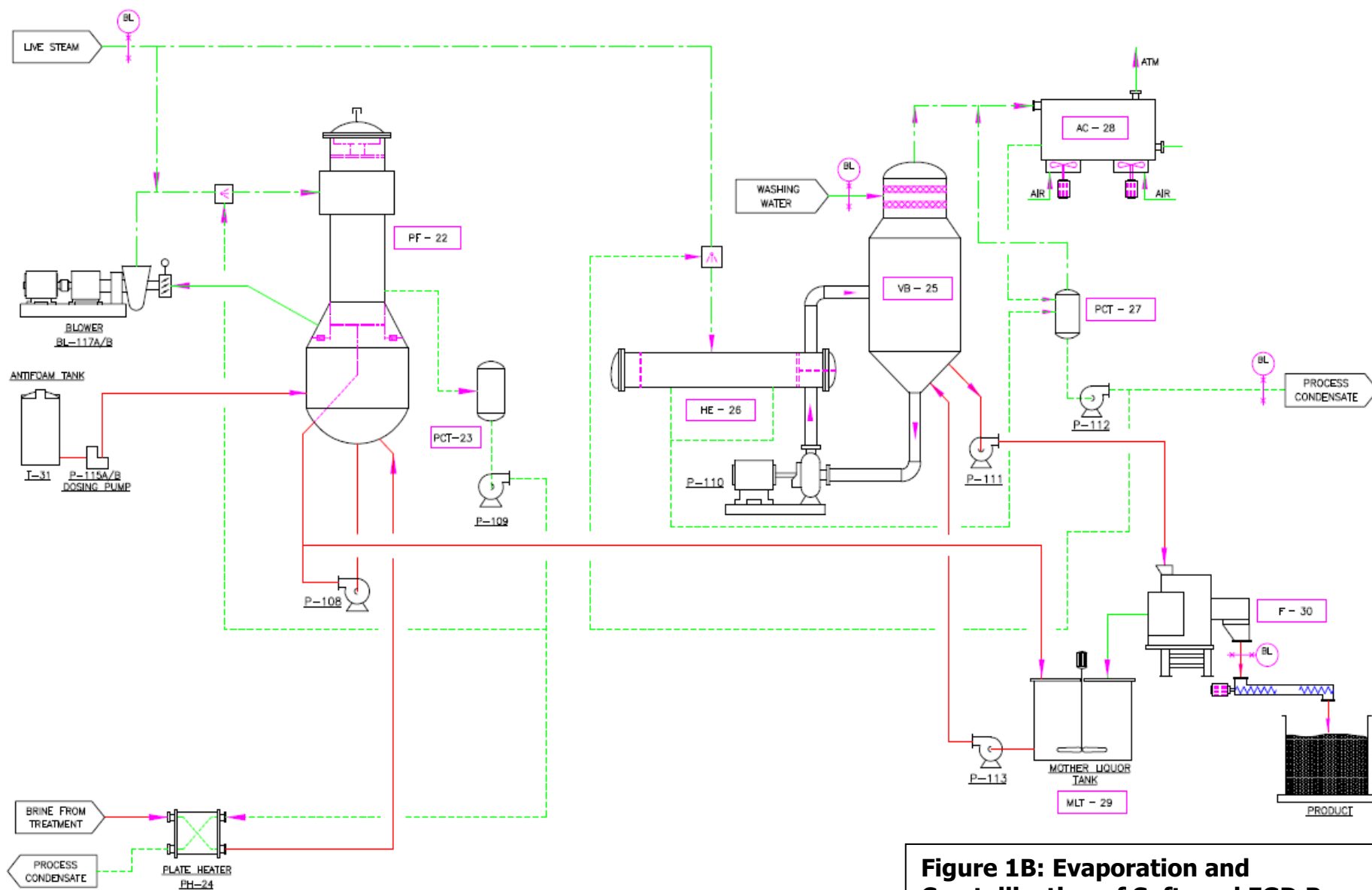
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Figure 1B: Evaporation and Crystallization of Softened FGD Purge

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To understand the principle behind cold crystallization, we will use the example of a ZLD wastewater treatment plant for FGD limestone scrubber purge. Cold crystallization of purge streams from wet scrubbers can be effected using no chemicals and only electric power using a forced circulation crystallizer with a closed cycle heat pump and a solids dewatering device as shown in the flow diagram in Figure 2.

In our example, an FGD scrubber using limestone discharges a wastewater at a temperature of 55°C with the composition given in Table 1 below.

Table 1
Limestone Based FGD Wastewater
Composition at 55°C

Component	Unit	Typical value
Calcium as Ca	mg/l	4250
Magnesium as Mg	mg/l	950
Sodium as Na	mg/l	590
Potassium as K	mg/l	25
Iron as Fe	mg/l	15
Chloride as Cl	mg/l	10000
Sulfate as SO4	mg/l	1320
Nitrate as NO3	mg/l	90
Fluoride as F	mg/l	12
Silica as SiO2	mg/l	28
Total suspended solids	mg/l	5000

Let us assume that we will use a cold crystallizer in which the solution boils at the same temperature as the scrubber water feed, namely 55°C, to avoid the need for a preheater (since the solution is saturated in gypsum). The FGD wastewater is mixed with the mother liquor discharged from the centrifuge and the mixture is introduced into the boiling chamber of the crystallizer. The raw feed and returned mother liquor mix with the recirculating brine in the crystallizer.

Sufficient heat to boil the brine is supplied in the crystallizer forced circulation heat exchanger. The heated brine flows back to the boiling chamber, where it flash boils. As the solution concentrates by evaporation of water, crystals of solids which have supersaturated in the mother liquor grow inside the boiling chamber. The evaporated water vapor flows into the condenser, where it gives up its latent heat of vaporization and condenses. The condensate is extracted from the condenser by a pump and any non-condensable gases are extracted by the vacuum system. The concentrated slurry is pumped from the boiling chamber to a dewatering device such as a centrifuge or pressure filter, which separates the solids from the mother liquor which flows back to the crystallizer boiling chamber. The dewatered solids are collected for disposal.

The heat required to boil the liquid and the cooling necessary to condense the water vapor are supplied by a closed cycle heat pump. Several different refrigerants can be used as the working fluid in the heat pump including ammonia or hydrofluorocarbons. The refrigerant fluid is heated by compressing it in the refrigerant compressor. Electrical energy which drives the compressor motor provides the work that is the source of heat for the crystallizer. Part of the heat imparted to the refrigerant by the compressor is transferred to the process liquor in the crystallizer heat exchanger by the partial condensation of the refrigerant. A water-cooled heat exchanger completes the condensation of the refrigerant and subcools it; the heat removed from the refrigerant is released to the environment. The liquid refrigerant flows through an expansion valve into the condenser, where it evaporates by heat which is transferred from condensing water vapor from the crystallizer. The cycle is closed as the refrigerant flows back to the compressor.

Figure 2
Flow Diagram of Cold Crystallizer Using Heat Pump
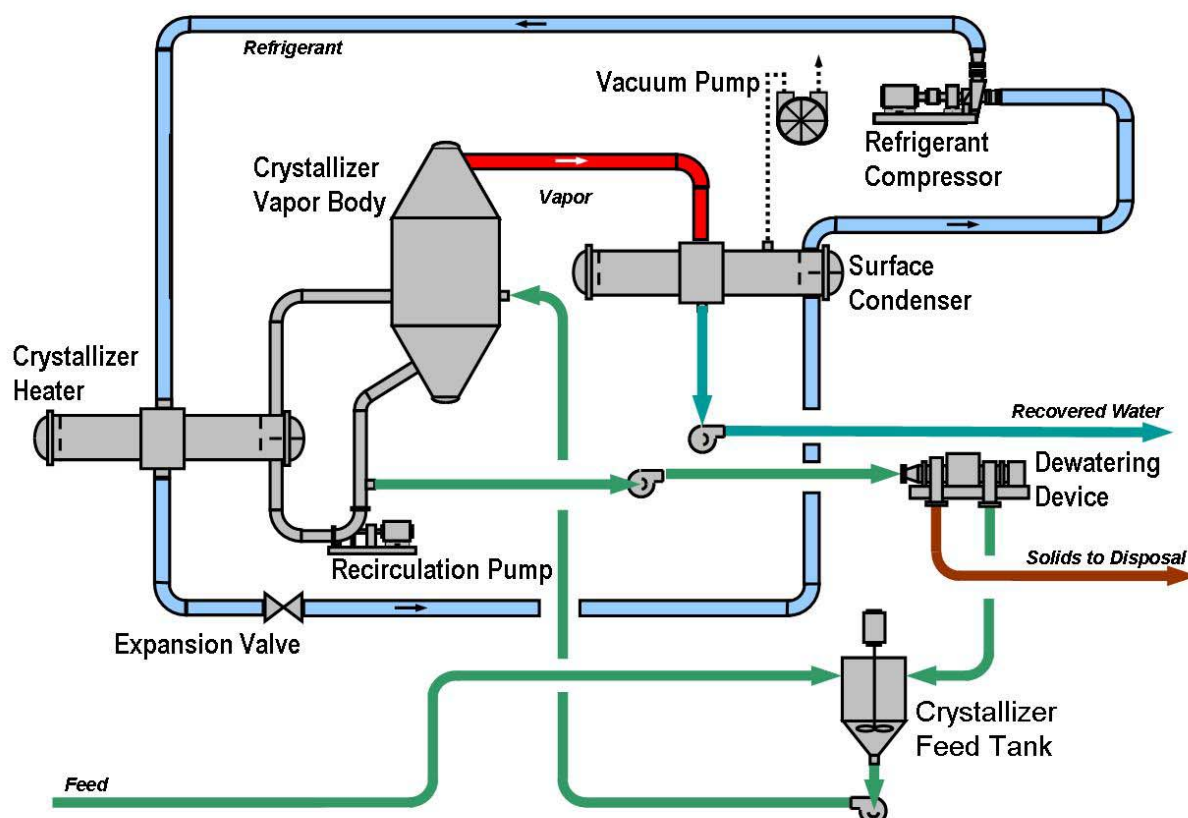
Looking at the composition of the scrubber wastewater given in Table 1, we can see that the solution is mainly calcium chloride with lesser amounts of magnesium, sodium, potassium, and iron chlorides and it is saturated in calcium sulfate and calcium fluoride. Since the purge is generally taken from the gypsum dewatering steps in the scrubber, the suspended solids are likely gypsum ($CaSO_4.2H_2O$). As water evaporates at 55°C from the scrubber wastewater with the composition given in Table 1, and concentration occurs, gypsum and calcium fluoride (CaF_2) will begin to precipitate immediately since the feed solution is saturated with these minerals. Upon further concentration, sodium chloride (NaCl) will begin to precipitate when its saturation limit is reached. The solubility of NaCl in calcium chloride solution is quite low and can be estimated in first approximation from the phase diagram of pure $CaCl_2/NaCl/H_2O$ -- about 1% NaCl in 57% $CaCl_2$ at 50°C according to The International Critical Tables, Vol. IV, p. 312.

When the gypsum, calcium fluoride, and sodium chloride have been depleted in the solution due to precipitation, the remaining solution is approximated by a mixture of

calcium chloride, magnesium chloride, and potassium chloride. To understand the behavior of this solution, we refer to the phase diagram at 55°C for the system $CaCl_2$/$MgCl_2$/KCl/H_2O from Seidell Vol. II, p. 140. To simplify the analysis, the phase diagram is presented in Figure 3 as a Janecke projection which represents the composition of the system in terms of the salts present, but excludes the water. At any point in the diagram, the mole percents of the three salts, $CaCl_2$, $MgCl_2$, and KCl, add up to 100%.

The Janecke projection in Figure 3 shows several regions. Each region represents a solution that is saturated with the salt of the composition labeled on that region. The largest region on the left is occupied by KCl, then a smaller field by the double salt carnallite ($MgCl_2.KCl.6H_2O$) and an even thinner stripe by the double salt tachyhydrite ($CaCl_2.2MgCl_2.12H_2O$); in the MgCl2 corner bischoffite ($MgCl_2.6H_2O$) and in the CaCl2 corner calcium chloride dihydrate and along the KCl-$CaCl_2$ axis a double salt of calcium chloride and potassium chloride.

For the FGD wastewater with the analysis given in Table 1, the point (**a**) representative of the feed composition lies in the tachyhydrite field, i.e. upon concentration tachyhydrite will precipitate and the point representative of the composition of the solution will move along a ray joining the point corresponding to the molar composition of tachyhydrite (**b**) to the feed (**a**) away from the tachyhydrite point (**b**). Depending on the ratio of K/Ca, the ray will intersect the solubility line between tachyhydrite and calcium chloride dihydrate (**c**) or the solubility line between tachyhydrite and carnallite, at which point the new salt will co-precipitate. The final mother liquor composition will be at the point (**d**) where tachyhydrite, carnallite and calcium chloride dihydrate coexist. This is an invariant point; i.e., the composition of the mother liquor is
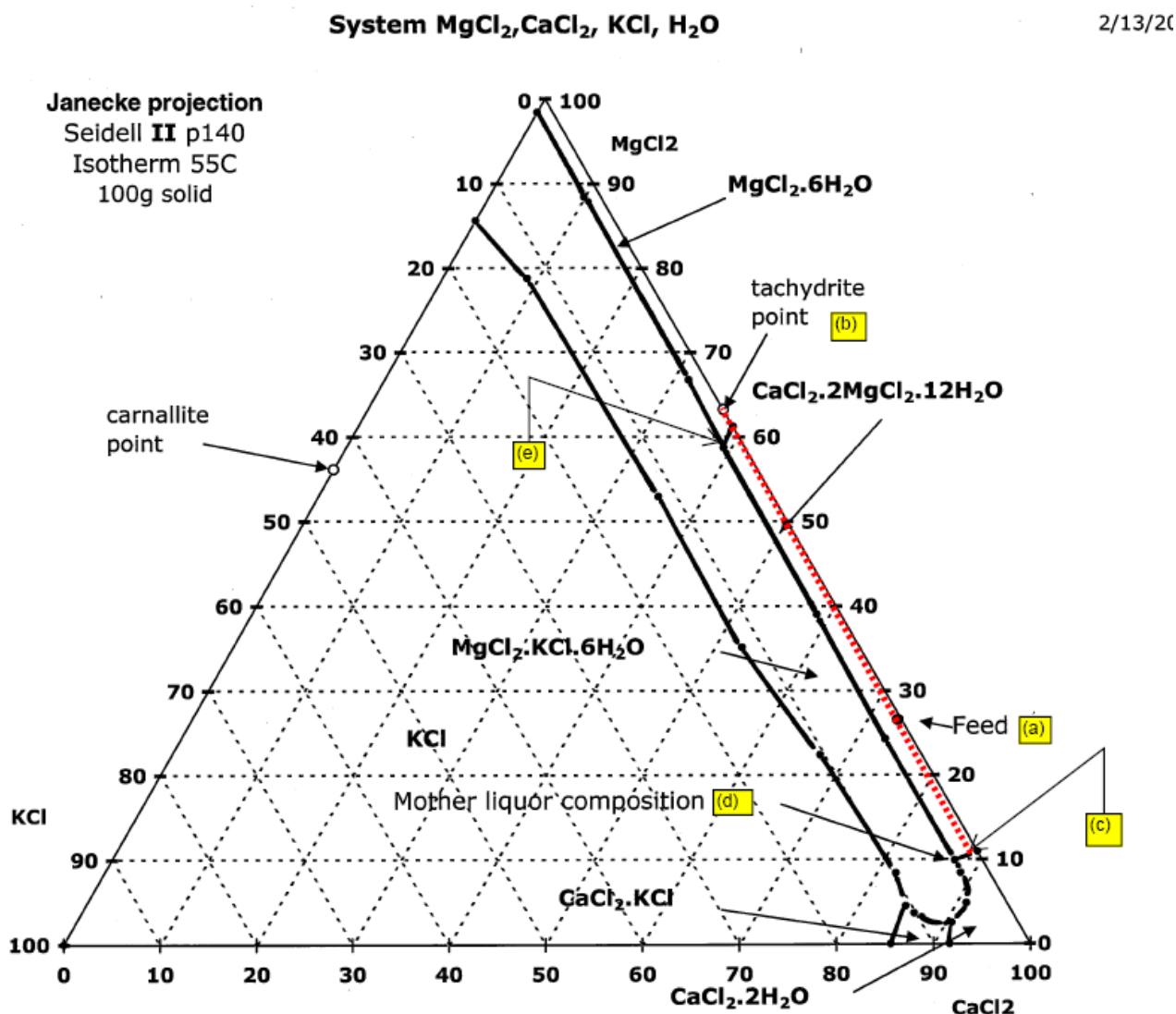
only dependent on the temperature of the solution.

Similarly if the solution is richer in magnesium than in calcium (sometimes seen when dolomitic limestone is used as the sorbent in the scrubber), the end mother liquor composition will be where tachyhydrite, carnallite and bischoffite coexist (**e**)

At steady state, all the solid salts are stable phases and will continue to precipitate. The final mother liquor concentration will remain that defined by the invariant point (**d**). A mixture of crystals of these solid salts can be grown in the crystallizer and separated in a centrifuge or other solids separation device. These hydrated salts grow relatively large making the separation of a cake with low residual moisture possible. The mother liquor is recycled to the crystallizer for further concentration and crystallization. The wet cake thus produced can be disposed of as is, and does not need further drying: upon cooling calcium chloride dihydrate will convert to the tetrahydrate and will absorb the residual free water. These salts, however, are hygroscopic, i.e., they absorb moisture from the environment including humidity in the air. Therefore the wetcake requires special handling to limit exposure to rain, snow, and humid conditions.

At steady state and constant temperature of 55°C, the composition of the mother liquor is fixed and depends only on the temperature. Obviously, the relative proportion of the solid salts in the wet cake depends on the initial wastewater composition, but the composition of the mother liquor is known. Thus the physical properties of the mother liquor are known or can be estimated with reasonable accuracy. At 55°C a boiling solution in equilibrium with tachyhydrite, calcium chloride dihydrate, and carnallite has a

Figure 3
Janecke Projection of the System CaCl$_2$/MgCl$_2$/KCl/H$_2$O at 55° C

System MgCl$_2$,CaCl$_2$, KCl, H$_2$O   2/13/20

Janecke projection
Seidell **II** p140
Isotherm 55C
100g solid

MgCl2
MgCl$_2$.6H$_2$O
tachydrite point (b)
CaCl$_2$.2MgCl$_2$.12H$_2$O
carnallite point
(e)
MgCl$_2$.KCl.6H$_2$O
KCl
Feed (a)
Mother liquor composition (d)
(c)
CaCl$_2$.KCl
CaCl$_2$.2H$_2$O
CaCl2

boiling point elevation 35 degrees C less than at atmospheric pressure.

Besides a lower boiling point elevation, the lower operating temperature of 55°C results in a much lower acid hydrolysis rate for the calcium chloride and magnesium chloride in solution. The low temperature operation makes the selection of the materials of construction easier when dealing with mixtures of chloride salts which hydrolyze and produce HCl in the solution. Low operating temperature translates to a less aggressive solution and the material of construction need not be high nickel or high molybdenum alloys. In the potash industry, carnallitic liquors are handled at low temperatures in carbon steel or rubber lined steel equipment.

Figures 1A and 1B represent the typical flow diagram for current ZLD plants for FGD scrubber purge using a chemical softening process as pretreatment to an evaporator and crystallizer. We can see that if a cold crystallizer is used at the right process conditions, the softening plant (Fig. 1A) can be eliminated and the highly soluble salts can be precipitated under reasonable process conditions in the cold crystallizer. Depending on the flow of wastewater to be processed, it may be useful to retain the evaporator in the process scheme to efficiently evaporate a large portion of the water. However, the evaporator must be seeded to handle feed solution which is saturated in calcium sulfate, and the final concentration to be achieved in the evaporator must be less than the solubility limit of the sodium chloride. The only change required to the crystallization / solids separation process diagrammed in Fig. 1B is that a vacuum system and heat pump circuit must be added to the crystallizer to convert it to a cold process.

Besides the simplified flow scheme, the cold crystallization process results in substantial savings in CAPEX and OPEX, because eliminating the chemical softening step eliminates the cost of buying, shipping, storing, and handling of bulk reagents and also eliminates the dewatering, storage, transport, and disposal of the softener sludge.

The cold crystallization process will treat FGD wastewater or wastewater from other gas scrubbing operations, or landfill leachate, or any wastewater containing significant quantities of high solubility salts resulting in high boiling point elevation, or where corrosion is a concern. These waste streams can be evaporated to form stable solids using a closed cycle heat pump or other means to achieve a low boiling temperature in the crystallizer; thus,

(1) dispensing with the need to use chemicals to soften or otherwise condition the feed prior to evaporation,
(2) limiting the amount of solid to be disposed of to only that contained in the feed,
(3) operating at a predictable final concentration of mother liquor in spite of variations in feed composition,
(4) discharging the final solid product as a wet cake, not requiring any further drying in order to transport or dispose,
(5) recovering all the water contained in the feed at a good quality, except for that left in the wet cake,
(6) requiring no energy source other than electricity,
(7) having a smaller equipment footprint,
(8) using less noble materials of construction.